Public Review Draft

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Appendix 4

Literature Review

1. Background

As part of our evaluation of the potential air quality impacts of substituting ethanol-blended gasoline for MTBE-blended gasoline, we conducted a literature review of related programs implemented elsewhere. Our objective was to identify the directional change in key pollutants and hopefully an idea of the magnitude if possible. The main compounds of interest include ethanol, acetaldehyde, peroxyacetyl nitrate (PAN), methyl tert-butyl ether (MTBE), formaldehyde, benzene, and 1,3-butadiene. Other hydrocarbon compounds of interest include isobutene, toluene, xylene isomers, n-hexane, peroxypropionyl nitrate (PPN), and four alkylates (2-methylpentane, 3-methylpentane, methylcyclopentane, 2,2,4-trimethylpentane).

Ethanol has been a major component of light-duty vehicle fuels in several states in the United States including Alaska, Arizona, Colorado, and New Mexico. In Brazil, either neat (100%) ethanol or gasohol (a mixture of ethanol and gasoline) has been used as a fuel since 1979. The impacts of ethanol-blended fuel on vehicle emissions as well as air quality have been studied in Denver, Albuquerque, and cities in Brazil. The primary focus of these studies was on the change in ambient levels of acetaldehyde and PAN. Acetaldehyde is a combustion product emitted from ethanol-fueled engines and a major oxidation product from atmospheric reaction of ethanol. PAN formation in the atmosphere can be enhanced by the increase in ambient acetaldehyde concentrations.

A total of sixteen papers and reports were reviewed, of which nine provided information pertinent to the situation in California. The remaining studies were not as useful because they did not include a before and after study or they did not include ambient air quality impacts. The studies that provided the most insight covered three geographical areas. These are briefly summarized below. A complete list of references is included at the end of this appendix.

2. Denver, Colorado

The Denver metropolitan area is the first region in the United States to implement the use of oxygenated fuel in an effort to reduce ambient carbon monoxide (Anderson et al., 1994). This program has been mandated since the beginning of 1988 and the majority of the fuel sold contained 8% MTBE-based with the rest being a 10% ethanol blend. Since then, the additive used has gradually shifted from largely MTBE to largely ethanol. By the winter of 1996/97, nearly all of the fuel sold was ethanol-blended fuel. Several studies have been conducted by Anderson and his colleagues at the University of Colorado (1994, 1996, 1997) on the air quality impacts of oxygenated fuels in Denver, with the focus on the change in ambient levels of aldehydes. The results of the earlier study (Anderson et al., 1994, 1996) covered the period 1988 to 1993. During this period the percent of oxygen in the fuel was continuously increased from 1.5 to 2.6%. That study showed that motor vehicle emissions were the major source of aldehydes and that the increase in average winter formaldehyde concentration from 1988 to 1993 was due to the increased percentage of oxygenate. However, the change in acetaldehyde was not statistically significant during this period. More recently, Anderson et al. (1997) reported that the concentrations of formaldehyde and acetaldehyde during the winter of 1995/96 when nearly all of the fuel was blended with ethanol were not significantly different from those measured during the winter of 1988/89 when 95% of the fuel was blended with MTBE. It was concluded that the photochemical production and destruction of these carbonyl compounds suppress the emissions effect. Unfortunately, ambient aldehyde concentrations were not measured prior to the introduction of oxygenated fuel in 1988 so a study of conditions before and after the introduction of oxygenates could not be conducted.

3. Albuquerque, New Mexico

Albuquerque is one of the U.S. urban areas mandated to use oxygenated gasoline fuel blends for improving air quality during the winter months. Over 99% of the fuel being sold contains 10% ethanol in the winter. Gaffney et al. (1997) have examined the air quality impacts of ethanol-gasoline fuel blends by measuring the ambient concentrations of PAN and aldehydes in the summer of 1993 (prior to the introduction of ethanol-containing fuel) and in the winters of 1994 and 1995 (after the introduction of ethanol-containing fuel). Compared to the summertime data, a 10% acetaldehyde increase during one winter but a significant decrease (lower by a factor of five) in the other winter was observed. The study also showed that an increase of PAN by a factor of two and four respectively was observed in both winters which the authors attributed to the use of ethanol fuel. However, as pointed out by Whitten (1998), the study conducted by Gaffney et al. (1997) is not a convincing case for demonstrating the air quality impact of ethanol fuel. The major arguments are the lack of control conditions (i.e., no control data for pre-ethanol wintertime conditions) and meteorological variation. Average concentrations of PAN varied by a factor of two between the two winters, largely due to meteorology.

4. Brazil

Brazil is the only country in the world where a national, large-scale ethanol fuel program has been implemented. The ethanol fuel was first introduced in 1979 and its use has increased steadily since then. In 1997, approximately nine million automobiles in Brazil ran on a gasohol fuel (22% ethanol-blended fuel) and another four million ran on neat ethanol (Grosjean 1997). Several studies on air quality have been conducted since the introduction of ethanol fuel. Grosjean et al. (1990) have measured ambient concentrations of aldehydes, in three major urban cities of Brazil: San Paulo, Rio de Janeiro, and Salvador from 1986 to 1988 and reported that acetaldehyde was the most abundant carbonyl in terms of its maximum concentration (35 ppb), followed closely by formaldehyde (34 ppb). The results also showed that acetaldehyde concentrations in urban areas of Brazil were substantially higher than those measured elsewhere in the world, most likely caused by large-scale use of ethanol as a vehicle fuel. In contrast, the ambient levels of formaldehyde showed a small increase compared to those measured elsewhere. More recently, de Andrade et al. (1998) reported that the concentrations for formaldehyde and acetaldehyde measured in Salvador, Brazil ranged from 0.20 to 80 ppb and from 0.40 to 93 ppb, respectively. Because of high levels of ambient acetaldehyde, up to 5 ppb of PAN--the photochemical product of acetaldehyde--was observed in the atmosphere (Tanner et al., 1988). These observations also agreed with model calculations of the photochemical processes. In addition, Grosjean et al. (1998b) measured ambient concentrations of ethanol and MTBE in Porto Alegre, Brazil from March 1996 to April 1997. Ambient levels of ethanol and MTBE ranged from 0.4 to 68.2 ppb and 0.2 to 17.1 ppb, respectively. Since there were no ambient data available prior to the use of ethanol fuel, the direct impact on air quality before and after the use of ethanol fuel could not be evaluated.

In summary, the studies of the impact of the use of ethanol fuel on air quality conducted in Denver, Albuquerque, and Brazil are not comprehensive but provide useful insight. The air quality impact is substantial only in the area where the fuels being used contain either neat ethanol or 22% ethanol such as in Brazil.

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